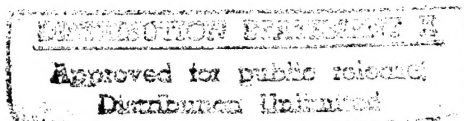


Quarterly Technical Report

Selected Energy Epitaxial Deposition and Low Energy Electron Microscopy of AlN, GaN and SiC Thin Films

Supported under Grant #N00014-95-1-0122
Office of the Chief of Naval Research
Report for the period 4/1/96-6/30/96



R. F. Davis, H. H. Lamb[†] and I. S. T. Tsong*,
E. Bauer*, E. Chen[†], R. Chilukuri[†], R. B. Doak*, J. L. Edwards*,
N. Freed*, J. Fritsch, S. Horch*, C. Linsmeier*, M. Meloni*,
K. E. Schmidt*, V. Torres,* and S. Zhang
Materials Science and Engineering Department

[†]Chemical Engineering
North Carolina State University
Campus Box 7907
Raleigh, NC 27695-7907

and
*Department of Physics and Astronomy
Arizona State University
Tempe, AZ 85287-1504

19960809 140

June, 1996

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June, 1996	3. REPORT TYPE AND DATES COVERED Quarterly Technical 4/1/96-6/30/96	
4. TITLE AND SUBTITLE Selected Energy Epitaxial Deposition and Low Energy Electron Microscopy of AlN, GaN, and SiC Thin Films			5. FUNDING NUMBERS 1213801--01 312 N00179 N66020 4B855	
6. AUTHOR(S) R. F. Davis, H. H. Lamb and I. S. T. Tsong				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) North Carolina State University Hillsborough Street Raleigh, NC 27695			8. PERFORMING ORGANIZATION REPORT NUMBER N00014-95-1-0122	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Sponsoring: ONR, Code 312, 800 N. Quincy, Arlington, VA 22217-5660 Monitoring: Administrative Contracting Officer, Regional Office Atlanta Regional Office Atlanta, 101 Marietta Tower, Suite 2805 101 Marietta Street Atlanta, GA 30323-0008			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The ionicity of the III-V nitrides requires going beyond the original approach of the multicenter tight-binding method based on the Harris functional for the total energy. By including a self-consistent treatment of the electronic charge density in the formalism, a significant improvement of the static and dynamical properties calculated for GaN and AlN can be achieved. The extension of the generalized <i>ab initio</i> tight-binding scheme to slab calculations makes it necessary, to optimize the updating procedure for the output charge density in the self-consistent cycle, so that convergence is achieved already after a small number of iterations. The assembly of a supersonic molecular beam source has been completed. Beam intensities as a function of flow through the nozzle have been determined to be in the range of 2×10^{19} atoms/srrad/s. An arc-heated nozzle for the production of atomic N beams has been designed and is being fabricated. The selected energy epitaxial deposition (SEED)/x-ray photoelectron spectroscopy (XPS) facility is complete. Exposure of oxygen-passivated Al and sapphire(0001) at 300°C to a remote nitrogen plasma containing primarily electronically excited molecular N ₂ species results in partial nitridation of the surfaces, as evidenced by Auger electron spectroscopy (AES) and XPS. Determination of the alignment and energy distribution of the ion beams of two colutron units is underway.				
14. SUBJECT TERMS III-V nitrides, ionicity, electronic charge density, tight-binding, molecular beam source, selected energy epitaxial deposition, nitrogen plasma, colutron			15. NUMBER OF PAGES 17	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLAS	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLAS	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLAS	20. LIMITATION OF ABSTRACT SAR	

Table of Contents

I.	Introduction	1
II.	<i>Ab Initio</i> Calculations of the Structure and Growth Properties of III-V Nitrides	4
III.	Testing of a NH ₃ Seeded He Supersonic Molecular Beam Source for Growth of AlN and GaN Layers	6
IV.	Selected Energy Epitaxial Deposition (SEED) of III-V Nitride and SiC Thin Films	9
V.	Deposition by Dual Colutron Ion Beams	16
VI.	Distribution List	17

I. Introduction

The realized and potential electronic applications of AlN, GaN and SiC are well known. Moreover, a continuous range of solid solutions and pseudomorphic heterostructures of controlled periodicities and tunable bandgaps from 2.3 eV (3C-SiC) to 6.3 eV (AlN) have been produced at North Carolina State University (NCSU) and elsewhere in the GaN-AlN and AlN-SiC systems. The wide bandgaps of these materials and their strong atomic bonding have allowed the fabrication of high-power, high-frequency and high-temperature devices. However, the high vapor pressures of N and Si in the nitrides and SiC, respectively, force the use of low deposition temperatures with resultant inefficient chemisorption and reduced surface diffusion rates. The use of these low temperatures also increases the probability of the uncontrolled introduction of impurities as well as point, line and planar defects which are likely to be electrically active. An effective method must be found to routinely produce intrinsic epitaxial films of AlN, GaN and SiC having low defect densities.

Recently, Ceyer [1, 2] has demonstrated that the barrier to dissociative chemisorption of a reactant upon collision with a surface can be overcome by the translational energy of the incident molecule. Ceyer's explanation for this process is based upon a potential energy diagram (Fig. 1) similar to that given by classical transition-state theory (or activated-complex theory) in chemical kinetics. The dotted and dashed lines in Fig. 1 show, respectively, the potential wells for molecular physisorption and dissociative chemisorption onto the surface. In general, there will be an energy barrier to overcome for the atoms of the physisorbed molecule to dissociate and chemically bond to the surface. Depending upon the equilibrium positions and well depths of the physisorbed and chemisorbed states, the energy of the transition state E^* can be less than zero or greater than zero. In the former case, the reaction proceeds spontaneously. In the latter case, the molecule will never proceed from the physisorbed state (the precursor state) to the chemisorbed state unless an additional source of energy can be drawn upon to surmount the barrier. This energy can only come from either (1) the thermal energy of the surface, (2) stored internal energy (rotational and vibrational) of the molecule, or (3) the incident translational kinetic energy of the molecule. Conversion of translational kinetic energy into the required potential energy is the most efficient of these processes. Moreover, by adjusting the kinetic energy, E_i , of the incoming molecule, it is possible to turn off the reaction ($E_i < E^*$), to tailor the reaction to just proceed ($E_i = E^*$), or to set the amount of excess energy to be released ($E_i > E^*$). The thrust of the present research is to employ these attributes of the beam translational energy to tune the reaction chemistry for wide bandgap semiconductor epitaxial growth.

The transition state, E^* , is essentially the activation energy for dissociation and chemisorption of the incident molecules. Its exact magnitude is unknown, but is most certainly

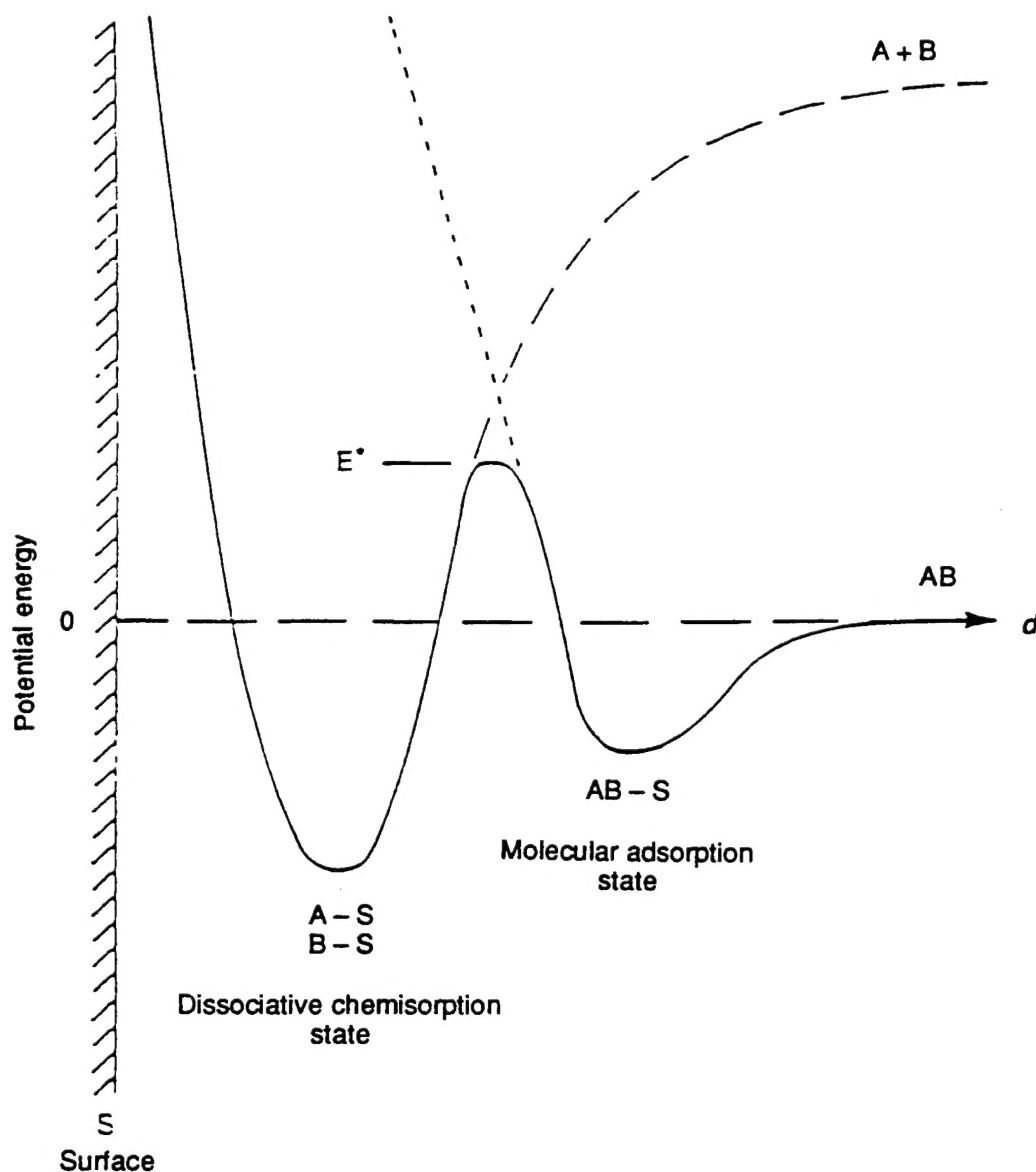


Figure 1. Schematic potential energy diagram of an activated surface reaction involving a molecularly physisorbed precursor state [from Ref. 1].

lower than the dissociation energy of the free molecule. It does not necessarily follow, however, that any kinetic energy above E^* will promote high-quality epitaxial growth of GaN. One must take into consideration another energy threshold, E_d , beyond which the kinetic energy of the incident flux will cause damage to the epitaxial film being synthesized. A typical E_d threshold value is approximately five times the bandgap of the crystal and in the case of GaN, $E_d \approx 18$ eV.

From the above consideration, it is clear that the key to high quality epitaxial growth is to be able to tune the energy of the incoming flux species over a range of energies defined by the window between E^* and E_d . Since the window is quite restrictive, i.e. 1-20 eV, it is essential

that the energy spread of the flux species must be small, i.e. the flux species should ideally be monoenergetic. To this end, we employ Selected Energy Epitaxial Deposition (SEED) systems for the growth of AlN, GaN and SiC wide bandgap semiconductors. The SEED systems are of two types: (1) a seeded-beam supersonic free-jet (SSJ) and (2) a dual ion-beam Colutron. Both these SEED systems have the desirable property of a narrow energy spread of ≤ 1 eV.

Epitaxial growth using the seeded-beam SSJ involves a close collaboration between investigators at NCSU and Arizona State University (ASU). At ASU, the SSJ is interfaced directly into a low-energy electron microscope (LEEM) for the conduct of *in situ* studies of the nucleation and growth of epitaxial layers; while at NCSU, the SSJ systems are used to grow device-quality AlN, GaN and SiC for real applications. Exchanges in personnel (students) and information between the two groups ensures the achievement of desired results. The additional thin film growth experiments using dual-beam Colutrons and the theoretical studies referred to in this report are primarily conducted at ASU.

The research conducted in this reporting period and described in the following sections has been concerned with (1) modeling of the III-V nitrides using the multicenter tight-binding method including a self-consistent treatment of the electronic charge density in the formalism, (2) assembly and characterization of a supersonic molecular beam source, (3) the assembly of a new selected energy epitaxial deposition system for growth of GaN and SiC films, and (4) the assembly and beam characterization of two dual Colutron ion-beams. The following individual sections detail the procedures, results, discussions of these results, conclusions and plans for future research. Each subsection is self-contained with its own figures, tables and references.

1. S. T. Ceyer, Langmuir 6, 82 (1990).
2. S. T. Ceyer, Science 249, 133 (1990).

II. *Ab Initio* Calculations of the Structure and Growth Properties of III-V Nitrides

The *ab initio* multicenter tight-binding model of Sankey and Niklewski [1] has proven to be a reliable and fast method to study the static and dynamical properties of complex systems on the basis of molecular dynamics simulations. In most of the calculations, the Harris-Foulkes functional [2, 3] has been used to describe the total energy, with a representation of the input charge density by a sum of atomic-like charge densities. For systems with different atomic species, however, it is essential to treat the electrons in a self-consistent way, in order to obtain a correct description of the charge redistribution caused by the chemical environment, especially in the case of a significant difference in the electronegativity. The ionicity of the III-V compounds, therefore, requires going beyond the limitations of the original approach of the Harris functional.

Recently, Demkov and co-workers have generalized the tight-binding method of Sankey and Niklewski by including the charge transfer between the ions in a self-consistent fashion without losing the efficiency of the first-principles molecular dynamics simulation scheme [4]. This is achieved by extending the original Harris functional in a straight-forward way by introducing variable occupation numbers for the atomic orbitals and explicitly treating the long-range Coulomb interactions.

Preliminary results obtained for the lattice constant, the bulk modulus, and the optical phonon frequencies calculated for cubic GaN and AlN show that it is necessary to treat the III-V nitrides within the generalized *ab initio* tight-binding scheme. By using the original, non-generalized method, no minimum of the total energy can be found for GaN and AlN even by varying the lattice constant in a considerably large range about the experimentally determined values. In contrast to that, we obtain an energy minimum with an underestimation of the measured lattice constant of about six percent by theory, if the charge redistribution is calculated in a self-consistent way.

An advantage of the Harris functional in both its original, as well as in its generalized form, is the possibility of choosing an appropriate form of atomic input charge densities. The electronic eigenstates are described by a basis of pseudo-atomic orbitals (PAO) obtained from the pseudopotential calculation. In order to restrict the short-range interaction contributions to only a small number of neighboring atoms, the PAO's are constructed under the boundary condition that they vanish at and outside a predetermined cutoff radius r_C .

Due to the confinement, the PAO's are slightly excited yielding slightly contracted atomic charge densities. Remarkably, confined atomic orbitals improve significantly the accuracy of the Harris functional as they simulate the contraction of the atomic charge density as observed in solid-state systems. Provided that the confinement radius r_C is not too small, the results with

slightly excited PAO's do not critically depend on the exact value of r_C . For different species, however, the energy difference between the atomic orbitals of the contracted atoms has to be essentially the same as in free atoms. The current investigations concentrate on the determination of PAO's for Al, Ga, N, H, Si, and C that can be used in an arbitrary combination of two or more of these species without a significant loss of accuracy in the calculated properties.

In order to apply the generalized *ab initio* tight-binding formalism to the investigation of the growth properties of III-V nitrides, the method has to be extended to slab calculations. The existence of two surfaces in a slab supercell and charge transfer perpendicular to the plane of the crystal films increase the sensitivity of a self-consistent calculation to artificial charge sloshing, thus increasing the number of iterations needed for achieving self-consistency. By a careful treatment of the long-range contribution of the Coulomb interaction and by the use of an efficient extrapolation scheme for updating the output charge density for the next iteration [5], we have succeeded to minimize the number of iterations in the self-consistent cycle and hence the numerical labor.

After an extensive test of the generated PAO's based on a comparison of the theoretical results for the lattice constant, phonon frequencies, and other static properties with those obtained by experiment, we are able to investigate the structure and the growth of thin nitride films by performing calculations based on molecular dynamics simulations.

References

1. O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989).
2. J. Harris, Phys. Rev. B **31**, 1770 (1985).
3. W. Foulkes and R. Haydock, Phys. Rev. B **39**, 12520 (1989).
4. A. A. Demkov, J. Ortega, O. F. Sankey, and M. P. Grumbach, Phys. Rev. B **52**, 1618 (1995).
5. D. G. Anderson, J. Assoc. Comp. Mach. **12**, 547 (1965).

III. Testing of a NH_3 Seeded He Supersonic Molecular Beam Source for Growth of AlN and GaN Layers

A. Introduction

The nitride family of AlN, GaN and InN thin films have shown to be strong candidates for electronic and optoelectronic applications. With direct band gaps of 6.2 eV, 3.4 eV and 1.9 eV for AlN, GaN and InN respectively, solid solutions based on these materials provide for band gap modifications suitable for applications ranging from the red to the deep UV region of the spectrum [1]. Due to the high bond strength between N and H in NH_3 , the growth of III-V nitrides requires high substrate temperatures unless some other form of activation is present. Supersonic Molecular Beam Epitaxy (SMBE) has been shown to enhance the surface decomposition of silane and methane [2,3] because of the possibility of tuning the kinetic energy of these species to deform and cleave the bonds upon impact with the substrate. In addition the tuning of the energy spread is possible with SMBE. This is important in order to experimentally determine the chemisorption barriers for the systems being studied, as well as to provide species with high sticking coefficients at high enough intensities. SMBE is, therefore, a useful technique for the low-temperature growth of single-crystalline GaN films at suitable growth rates using NH_3 . A review of supersonic molecular beams can be found in Scoles [4].

The supersonic molecular beam source has been assembled and tested. Characterization of the beam intensity as a function of flow through the nozzle has been performed.

B. Experimental Procedure

The supersonic molecular beam source is shown in Fig. 1. As discussed in previous reports, the source consists of a source chamber where the gas expands forming a free jet expansion, pumped by a VHS-10 Varian diffusion pump backed by a Leybold WS 501 roots blower which is backed by a D65BCS Leybold mechanical pump. The free jet expansion is collimated by a skimmer (Beam Dynamics) with a 0.5 mm aperture. The beam is then differentially pumped by a VHS-4 diffusion pump with a 362-4 Varian cryotrap. The second differential pumping stage is pumped by an inverted magnetically suspended TMP 340M Leybold turbo pump. The gas source is controlled by a manifold described in previous reports. The beam intensity was measured as a function of flow out the nozzle using the Pitot technique. Briefly, the beam is directed at an isolated chamber and the equilibrium pressure resulting from thermal effusion out the chamber and the beam flux into the chamber is measured. The pressure is related to the intensity of the beam.

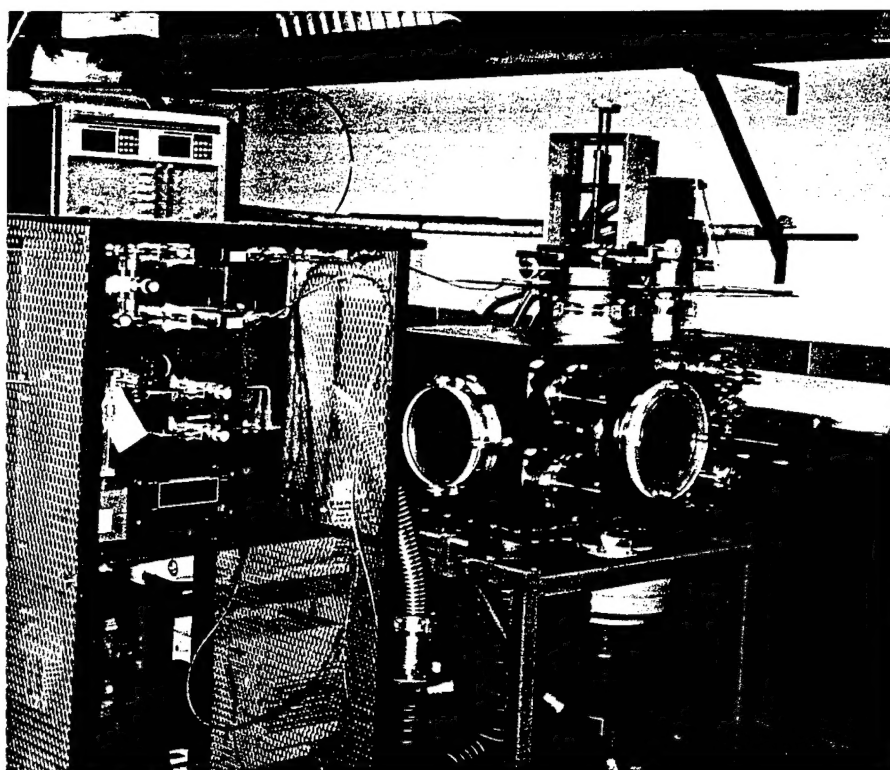


Figure 1. Supersonic molecular beam source at ASU.

C. Results and Discussion

The beam intensity as a function of flow through the nozzle is shown in Fig. 2 for a pure He beam. The beam intensity scales with the flow through the nozzle in a linear fashion as expected. A beam intensity of 2×10^{19} atoms/srrad/sec is obtained with a 500 sccm flow. For a 10% NH_3 beam, and a nozzle to sample distance of 20", this intensity corresponds to 1×10^{15} molecules/cm²/sec. The surface density of Si is 1.5×10^{15} atoms/cm². Therefore this source would expose a Si substrate to a monolayer of NH_3 molecules each second.

A student has been engaged to build an arc-heated nozzle source. This source will produce a N atom beam with an intensity in the order of 1×10^{19} atoms/srrad/sec. Such a source has an energy spread of 10 to 100 meV and a tunable energy of 0.5 to 10 eV. A design has been finalized and is under construction.

D. Conclusion

The assembly of a supersonic molecular beam source with an intensities in the range of 2×10^{19} atoms/srrad/sec. has been completed. An arc-heated nozzle for the production of a N atom beam is under construction.

E. Future Work

A chamber for preliminary depositions of AlN and GaN will be assembled. The depositions will provide for narrowing down the parameter space for growth of epitaxial films

in the LEEM. Two publications on the characterization of NH_3 seeded He free jets based on the experiments performed in the last year are being written and will be submitted.

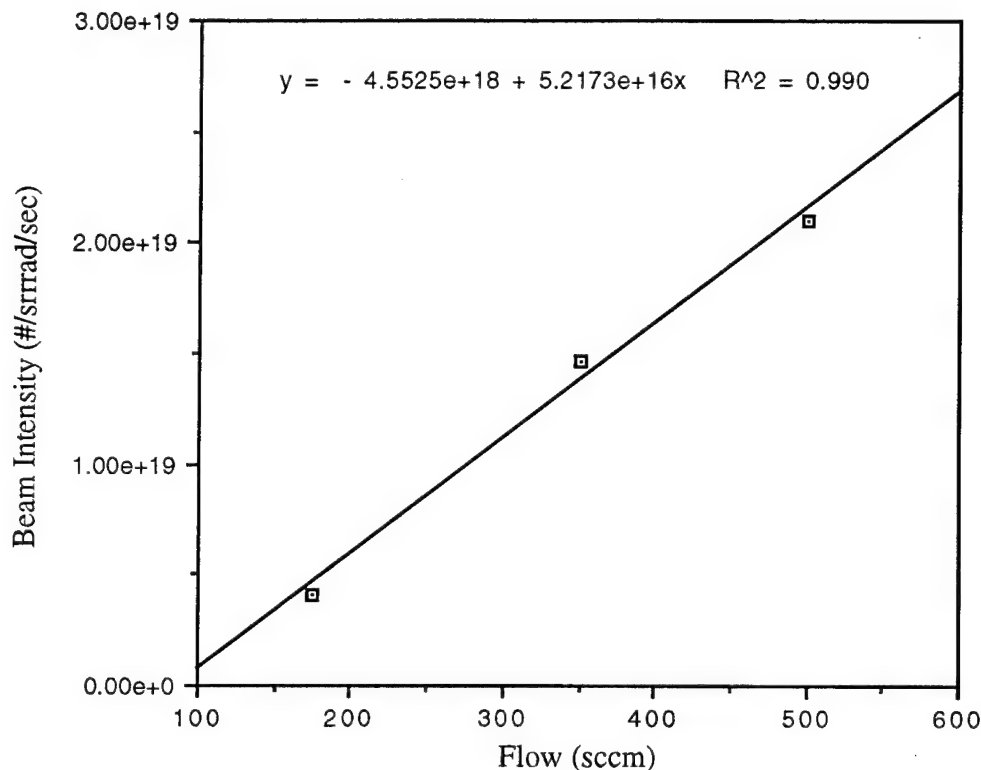


Figure 2. Beam intensity as a function of flow through the nozzle.

F. References

1. S. Strite and H. Morkoc, J. Vac. Sci. Technol., **B10**, 1237 (1992)
2. M. E. Jones, L. Q. Xia, N. Maity, J. R. Engstrom, Chem. Phys. Lett., **229**, 401 (1994)
3. S. T. Ceyer, J. D. Beckerle, M. B. Lee, S. L. Tang, Q. Y. Yang, M. A. Hines, J. Vac. Sci. Technol. A, **5**, 501, (1987)
4. D. R. Miller, Atomic and Molecular Beam Methods, Ch. 2, Ed. G. Scoles, Oxford University Press (1988)

IV. Selected Energy Epitaxial Deposition (SEED) of III-V Nitride and SiC Thin Films

A. Introduction

Gallium nitride is a promising wide bandgap semiconductor ($E_g = 3.4$ eV) for optoelectronic and high-temperature, high-frequency, microelectronic device applications. State-of-the-art GaN films ($\leq 10^8$ defects per cm^2) have been used to fabricate blue light emitting diodes (LEDs) and laser diodes. Moreover, GaN forms a continuous range of solid solutions with AlN (6.28 eV) and InN (1.95 eV), permitting the fabrication, via bandgap engineering, of laser diodes with tunable emission frequencies from covering the visible and UV regions.

Heteroepitaxial growth of high-quality monocrystalline GaN films has been problematic due to the lack of a suitable lattice-matched substrate and the thermodynamic instability of GaN under high-temperature, low-pressure chemical vapor deposition (CVD) conditions. Sapphire, the most common substrate, exhibits a 16% lattice mismatch at the GaN(0001)/sapphire(0001) interface; moreover, the thermal expansion coefficient of sapphire is 25% greater than that of GaN. Only by employing a low-temperature AlN or GaN buffer layer can one obtain monocrystalline films on sapphire with defect densities in the 10^8 - 10^9 cm^{-2} range.

Substrate temperatures in excess of 1000°C are required for growth of monocrystalline GaN films by halide or metal-organic CVD using NH_3 . Substrate thermal energy is required to overcome the activation barriers for dissociative chemisorption of NH_3 and adatom surface migration (lateral diffusion). Such high growth temperatures are undesirable as GaN is thermally unstable above 620°C *in vacuo* [1]. Plasma-assisted processes have been utilized to lower the GaN growth temperature to approximately 700°C , but ion-induced damage and oxygen contamination are often observed.

The use of energetic neutral beams of precursor molecules is an alternative approach to the epitaxial growth of GaN films at lower substrate temperatures. In selected energy epitaxial deposition (SEED), heavy reactant molecules are seeded in a supersonic expansion of light molecules and thereby accelerated to hyperthermal energies. The precursor molecules attain kinetic energies on the order of several eV which can provide the necessary energy for activated surface processes, such as dissociative chemisorption and adatom migration. Hence, in prospect, monocrystalline GaN films may be grown at much lower substrate temperatures by SEED than by conventional thermal techniques [2]. Moreover, energetic neutral beams with narrow energy distributions are useful in fundamental studies of wide bandgap semiconductor growth using *in situ* low-energy electron microscopy (LEEM) and other techniques.

As discussed in previous reports (Sept. 1995, Dec. 1995, Mar. 1996), GaN thin films can be deposited on sapphire(0001) via SEED at 600°C using V/III ratios ≥ 200 . From these

results, it is evident that incident translational energies of the precursors, NH_3 and triethylgallium (TEG), in the hyperthermal regime do influence GaN growth kinetics and film morphology. In particular, we infer that the tendency toward two-dimensional (2D) growth at low temperatures is enhanced by using a hyperthermal TEG molecular beam with a significant kinetic energy component parallel to the growth surface. Nonetheless, a two-step growth sequence involving a low-temperature buffer layer was required to achieve smooth, highly oriented GaN films on sapphire(0001). Consequently, in this reporting period we have begun to examine the surface preparation of sapphire for GaN growth.

Nitridation of sapphire using NH_3 or plasma-generated nitrogen species has been reported to improve the quality of subsequently deposited III-V nitride films.[3] A thin $\text{AlN}_x\text{O}_{1-x}$ layer has been shown to promote 2D growth, apparently by decreasing the interfacial free energy between the GaN film and the substrate. In this report, we examine the nitridation of oxygen-passivated Al and sapphire(0001) at low temperature using excited species from a remote RF nitrogen plasma. A detailed description of the recently completed SEED/XPS facility is also presented.

B. Experimental Procedure

SEED/XPS Facility. The multi-chamber SEED/XPS tool illustrated in Fig. 1 comprises a doubly differentially pumped molecular beam source, UHV-compatible growth chamber, x-ray photoelectron spectroscopy (XPS) chamber and two-stage load-lock/transfer line.

As shown in Fig. 2, the first differential pumping stage (nozzle chamber) is equipped with an 8000 L/s diffusion pump (Varian VHS-400) which is backed by a Roots blower (Tuthill 3206) and mechanical pump in series. The twin stainless steel nozzles feature replaceable laser-drilled apertures and 240-W cable heaters (Watlow) that allow heating to 800°C. Each nozzle is equipped with a xyz translation stage which is used for nozzle-skimmer alignment. The conical skimmers (Beam Dynamics) have 1-mm apertures. The second differential pumping stage (chopper chamber) is equipped with a 2000 L/s diffusion pump (Varian VHS-6) which is fitted with a fluid-cooled baffle and backed by a mechanical pump. The chopper chamber is separated from the growth chamber by a plate containing two 5-mm diameter, circular, beam-defining apertures. The molecular beam source and growth chamber, respectively, are equipped with a 100-mm rotating disk chopper (Globe Motors, B2000, 400 Hz) and quadrupole mass sensor (Hiden HAL/3F 301 PIC) for time-of-flight (TOF) velocity measurements. The quadrupole mass sensor is mounted on a rotatable table equipped with a z-motion stage for beam alignment. For TOF measurements, a photocoupler is used to provide a reference signal to a multichannel scaler card (EG&G Oxford Instruments MCS-II) installed in a PC. The base pressures of the nozzle and chopper chambers are 10^{-7} and 10^{-8} Torr, respectively.

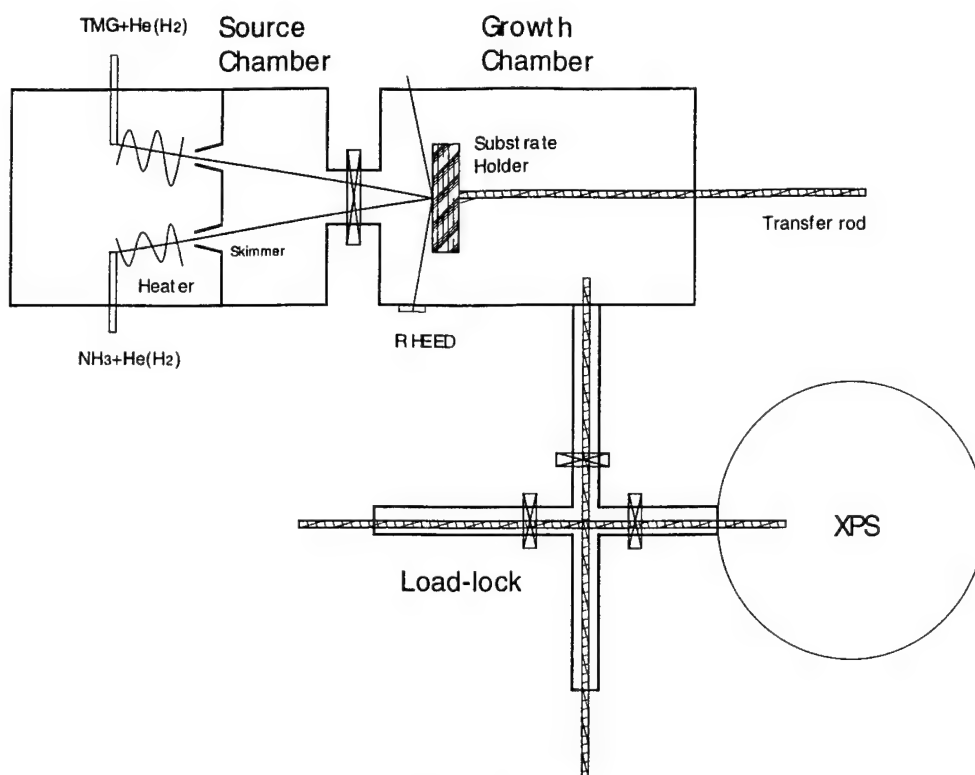


Figure 1. Schematic diagram of SEED/XPS facility.

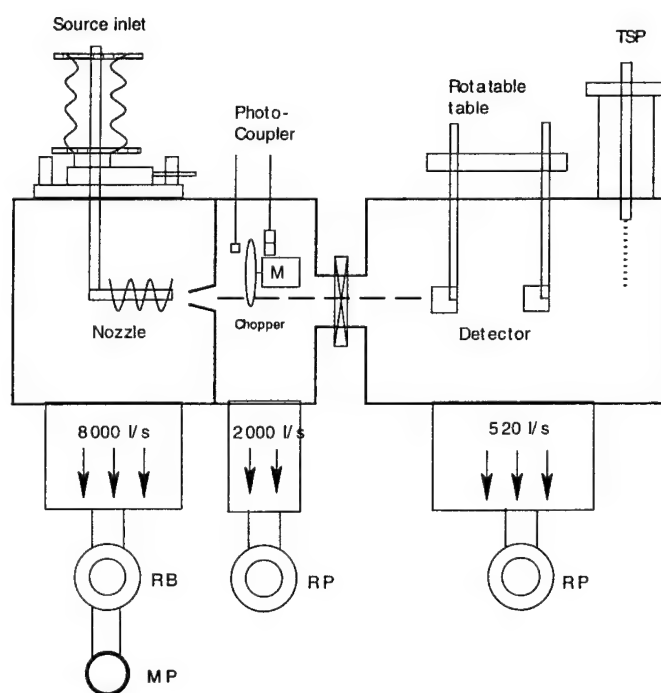


Figure 2. Schematic diagram of differentially pumped molecular beam source and SEED growth chamber, illustrating TOF velocity measurement capability.

The growth chamber is equipped with a hybrid turbomolecular/drag pump (Balzers 520M) and a PHI titanium sublimation pump (TSP), and has a base pressure of $<10^{-9}$ Torr. *In situ* reflection high-energy electron diffraction (RHEED) capability is provided by a Fisons LEG 110 15-kV electron gun and 100-mm Al-coated phosphor screen. Sample introduction is via a small load-lock chamber evacuated using a Drytel 31 molecular drag/membrane pump.

Subsequently, the sample is transferred to either the growth chamber or the UHV surface analysis chamber via a vacuum transfer line; the transfer line base pressure (10^{-9} Torr) is established using a cryopump (APD Cryogenics, APD-4).

The UHV surface analysis chamber is equipped with a PHI 3057 XPS system comprising a 10-360 spherical capacitor analyzer (SCA), Omni Focus III fixed-aperture lens, 16-element multichannel detector, and 257 DR11 PC interface card. A PHI 1248 dual-anode (Al/Mg) X-ray source is used. Non-destructive depth profiling is achieved by angle-resolved XPS (ARXPS): The sample is mounted on a tilt stage which is attached to a precision xyz -rotary manipulator (Thermionics) which is used to vary the photoelectron take-off angle. The analysis chamber is pumped by a Perkin-Elmer TNBX ion pump/TSP combination and has a base pressure of 2×10^{-10} Torr.

Remote Plasma Nitridation. Oxygen-Passivated Al. Substrates were prepared by depositing 1000 Å of Al on one side a 100-mm, double-polished Si(100) wafer. A 10 mm \times 20 mm piece was exposed to UV radiation in presence of air on both sides for 10 minutes each, to reduce organic contamination and grow a thin Al₂O₃ passivation layer. The sample was transferred to a UHV chamber equipped for Auger electron spectroscopy (AES) and Fourier transform infrared reflection-absorption spectroscopy (IRAS). AES was performed with a primary electron energy of 3 keV, and data was collected at 10 ms per each 1 eV step. An infrared spectrum of the passivated aluminum surface was obtained by reflection of a 12.8-mm IR beam from external surface at an 87° angle with respect to the surface normal. The specularly reflected beam was detected using a liquid-nitrogen-cooled MCT detector.

Thin AlN_xO_{1-x} films were grown on oxygen-passivated Al using a remote RF nitrogen plasma. Nitridation involved a 5-min exposure to plasma-excited nitrogen species at 300°C and 300 mTorr. The plasma was generated by passing 100 sccm of research-grade N₂ through a sintered alumina and applying 25 watts 13.56 MHz RF power. The sample was positioned 4 cm below the tube exit. Plasma-excited species were studied by optical emission spectroscopy (OES), using an EG&G PARC 1235 triple-grating spectrograph and 1435A 1024-element optical multichannel analyzer that was calibrated using Ar emission lines. Spectra were recorded using a 150 grooves/mm grating. The nitrided samples were characterized using AES and IRAS in the UHV chamber at the above-mentioned conditions.

Sapphire. A 5 x 5 mm² piece of <0001>-oriented sapphire was heated in a 1:1 mixture of H₂SO₄ and H₃PO₄ for 15 min at 80°C. Subsequently, the sample was rinsed with DI water,

etched in 10% HF for 10 min, rinsed in flowing DI water for 2 min and dried in flowing N₂. After *ex situ* cleaning the sample was characterized by XPS. The x-ray source (Mg anode) was operated at 15 kV and 300 W, and survey scans (0-1200 eV binding energy) were recorded using a pass energy of 117.4 eV. The sample was subsequently transferred to the remote plasma chamber and exposed to a nitrogen plasma under the above-mentioned conditions. After nitridation the sample was returned to the XPS chamber for analysis.

C. Results and Discussion

The SEED/XPS facility is complete, and initial vacuum shake-down is underway. Several leaks in the differential pumping stages were discovered and have been repaired. The TOF components have been tested using simulated high-frequency signals from a pulse generator. TOF measurements on TMG-seeded and TEG-seeded He supersonic molecular beams will commence after completion of the chopper motor driver circuitry (1 week). GaN deposition experiments using dual seeded molecular beams are planned immediately upon completion of the flow system (2-3 weeks).

Figure 3 shows the optical emission spectrum of a 25-W, 300 mTorr RF nitrogen plasma that was used in the nitridation experiments. The spectrum is dominated by peaks associated with the first-positive series of excited molecular N₂, which appear as broad multiple-peaked bands centered at 540, 590, 670, 755, and 880 nm. [5] The series of weak peaks between 350 and 420 nm is assigned to the second-positive series of molecular N₂. Peaks due to atomic N and N₂⁺ are very weak or absent. The production of significant quantities of N and N₂⁺ at higher RF powers will be the subject of future experiments.

Figure 4(a) is the AE spectrum of the Al surface after exposure to UV radiation in the presence of air. The surface is oxidized and relatively free of organic contamination. The Al(LVV) peak is split into two components: one at 38 eV associated with Al-O bonding and one at 56 eV associated with a mixture of Al-Al and Al-O bonding. The Al:O ratio in the near surface region (10-15 Å) is estimated at 4:1. The AE spectrum in Fig. 4(b) indicates that nitrogen plasma exposure at 300°C resulted in partial nitridation of the passivated Al surface. The surface atomic fractions of Al, O and N are estimated at 0.68, 0.18 and 0.10, respectively. A new Al(LVV) peak at 82 eV is observed. The small C and F peaks arise from contaminants desorbed from the walls of the remote plasma chamber; these will be eliminated in future experiments by chamber preconditioning. The IRAS spectrum does not contain any additional peaks after nitridation; however, OH stretching bands associated with bound water in the oxide passivation layer were eliminated.

The XPS spectrum of sapphire(0001) after *ex situ* cleaning (Fig. 5(a)) evidences the presence of Al, O and a small amount of adventitious carbon. The XPS spectrum of the sample

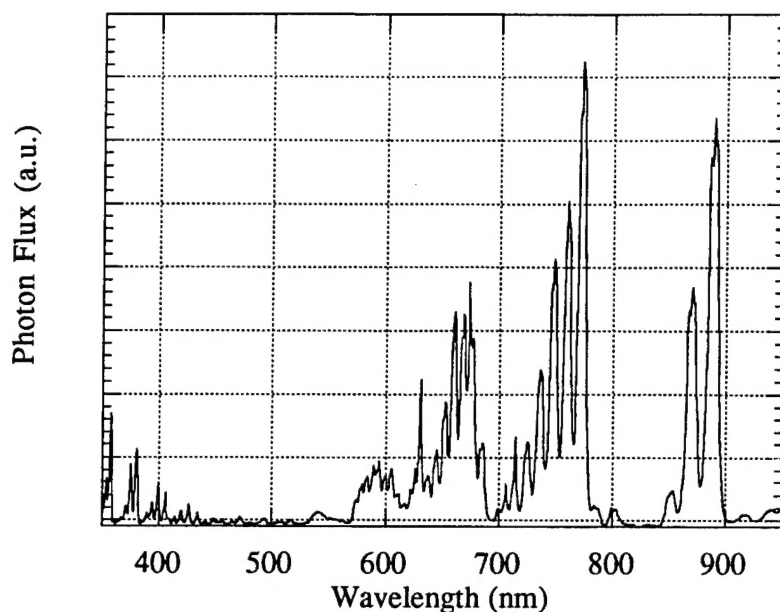


Figure 3. Optical emission spectrum of nitrogen plasma at an input power of 25 W and a chamber pressure of 300 mTorr.

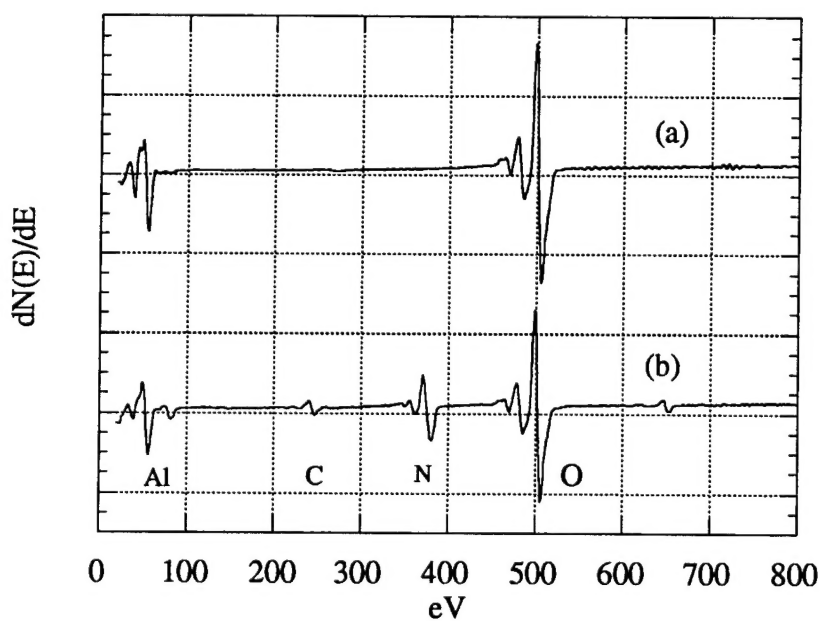


Figure 4. Auger Electron Spectra of (a) passivated Al surface, (b) Al surface after plasma nitridation.

after plasma nitridation at 300°C for 5 min (Fig. 5(b)) indicates partial conversion of the surface layer to AlN; however, the N(1s) peak is very small relative to the O(1s) peak. In addition, there is evidence of F arising from contamination in the plasma processing chamber.

D. Conclusions

Exposure of oxygen-passivated Al and sapphire(0001) at 300°C to a remote nitrogen plasma containing primarily electronically excited molecular N₂ results in partial nitridation of the surfaces. Remote plasma nitridation is potentially valuable for *in situ* surface preparation of sapphire prior to GaN SEED.

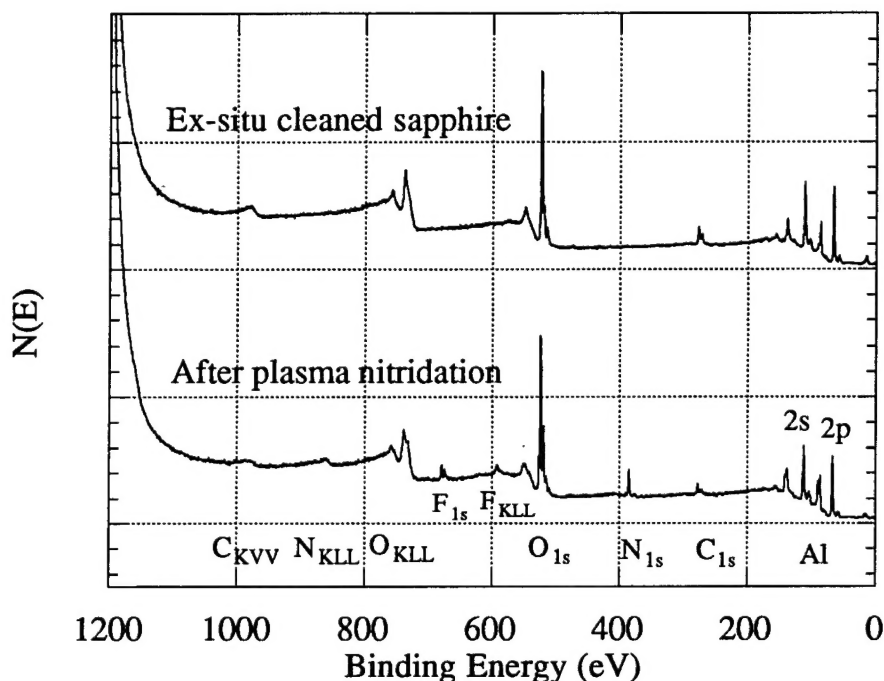


Figure 5. XPS binding energy spectra of sapphire(0001) after *ex situ* cleaning and after remote plasma nitridation.

E. Future Plans

- 1) GaN deposition experiments using dual seeded molecular beams.
- 2) TOF measurements on TMG-seeded and TEG-seeded He supersonic molecular beams.
- 3) Complete the investigation of sapphire nitridation by remote N plasmas.
- 4) Study nitridation of sapphire using seeded supersonic jets of NH₃.

F. References

1. S. Nakamura, Japan J. Appl. Phys. **30**, L1705 (1991).
2. M. R. Lorenz and B. B. Binkowski, J. Electrochem Soc. **109**, 24 (1962).
3. H. H. Lamb, K. K. Lai, V. Torres and R. F. Davis, in "Film Synthesis and Growth Using Energetic Beams," MRS Symp. Proc. **388** (1995).
4. K. Uchida, *et al.*, J. Appl. Phys. **79**, 3487 (1996) and references therein.
5. R. P. Vaudo, J. W. Cook, Jr. and J. F. Schetzina, J. Crystal Growth **138**, 430 (1994).

V. Deposition by Dual Colutron Ion Beams

A. Introduction

The objective of this work is to produce epitaxial SiC and GaN films by direct ion-beam deposition of two appropriate reacting chemical species, e.g. Si^+ and C^+ ions, and Ga^+ and N^+ ions. The deposition system consists of two Colutron ion beam units each equipped with a Wien Filter to select the mass of the desired ion, and an electrostatic deceleration lens to produce low-energy ions in the 10 eV range. The ion beams from the Colutron ion sources are near-monoenergetic, with an energy spread as low as 0.1 eV. The deposition system is further equipped with RHEED to monitor *in situ* film growth, and 4-grid retarding field analyzer to conduct LEED and AES to determine the surface structure and chemical composition of the films respectively, and an electrostatic energy analyzer to determine the energy distribution of the ions and also to characterize the composition of the top surface layer by ion-scattering spectrometry (ISS).

B. Experimental Procedure

We are in the process of aligning the ion beams from the two Colutron units. We are also using the electrostatic energy analyzer to analyze *in situ* the energy distribution of each individual ion beam. However, our progress is hampered by the breakdown of one of our turbomolecular pumps. We will resume our experiments as soon as the pump is repaired and returned to us.

C. Future Research and Goals

Both solid ions such as Ga^+ and Si^+ , and gaseous ions such as N_2^+ , N^+ and C^+ (from CO), will be extracted from the Colutron ion sources at initial energies of ~ 1 keV. The ions will then be decelerated to ~ 10 eV prior to arrival at the substrate surface. Film deposition of SiC and GaN on 6H-SiC(0001) substrates will proceed as soon as the measurements of the ion energy distributions are completed.

VI. Distribution List

Mr. Max Yoder Office of Naval Research Electronics Division, Code: 312 Ballston Tower One 800 N. Quincy Street Arlington, VA 22217-5660	3
Administrative Contracting Officer Office of Naval Research Regional Office Atlanta 101 Marietta Tower, Suite 2805 101 Marietta Street Atlanta, GA 30323-0008	1
Director, Naval Research Laboratory ATTN: Code 2627 Washington, DC 20375	1
Defense Technical Information Center Bldg. 5, Cameron Station Alexandria, VA 22304-6145	2